EMERGING CONTAMINANTS: POLY- & PERFLUOROALKYL SUBSTANCES (PFAS)

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OVERVIEW

01 What are PFAS?

- Sources
- Impacted facilities

02 Exposure and toxicity

03 Regulatory response

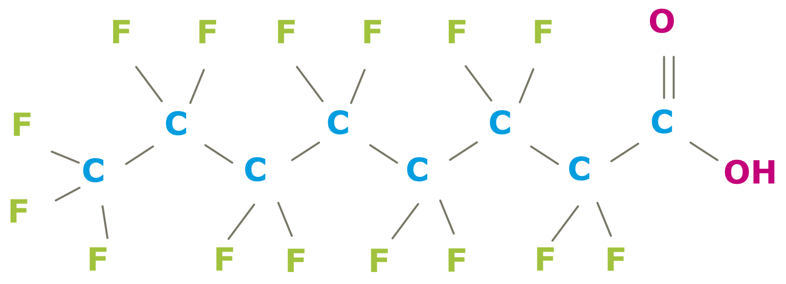
- State
- Federal
- International

04 Remediation options

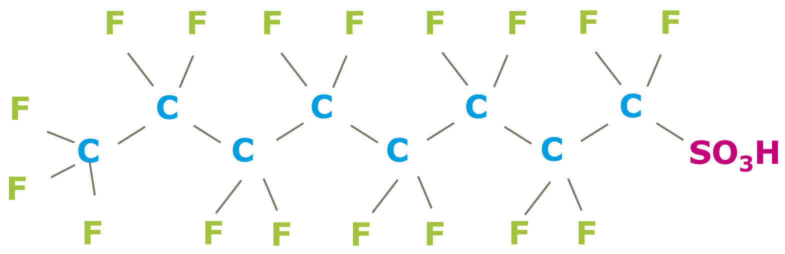
WHAT ARE PFAS?

POLY- & PERFLUOROALKYL SUBSTANCES

1. PFAS is the generic term for a large class of fluorinated chemicals
2. Used in a wide range of industrial applications, commercial products, and fire fighting foams
3. Unique because of their ability to repel oil, grease and water
4. Exceptionally stable, non-reactive chemicals, resistant to degradation and heat
5. Relatively mobile in the environment, moderately soluble
6. May be subject to long-range transport

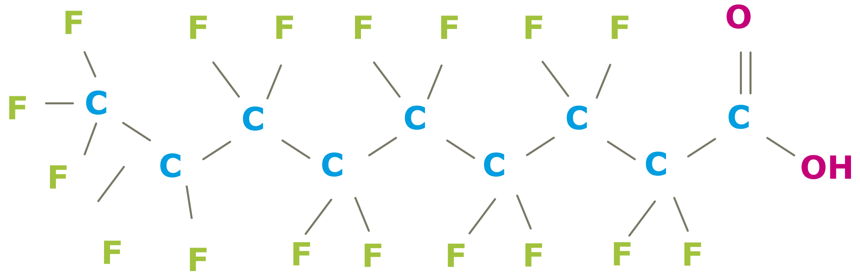


PFOA – perfluorooctanoic acid

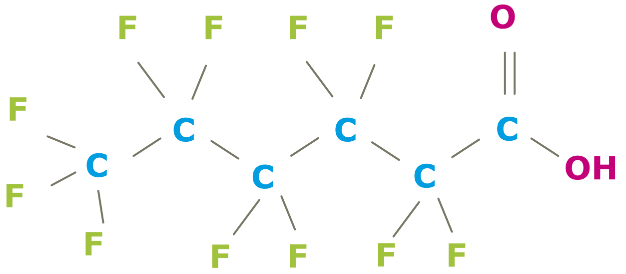


PFOS – perfluorooctanesulfonic acid

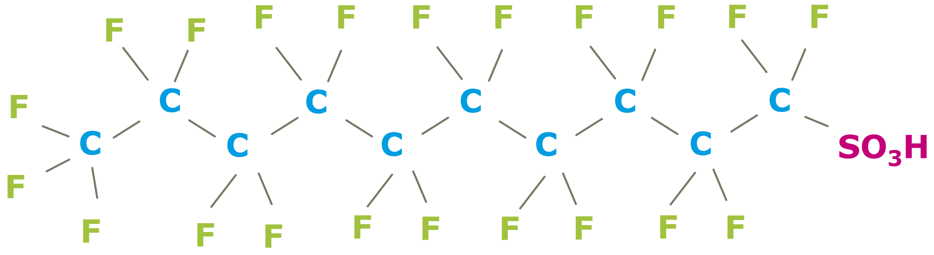
SHORT CHAIN VS LONG CHAIN COMPOUNDS



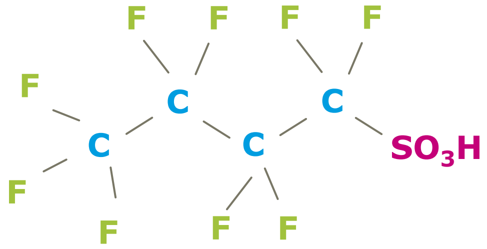
PFNA – perfluoro**nona**noic acid



PFHxA – perfluoro**hexa**noic acid



PFDS – perfluoro**decane**sulfonic acid



PFBS – perfluoro**butane**sulfonic acid

WHY THE INTEREST IN PFAS?

Widely distributed in the environment and attracting increasing attention over the past 20 years

Persistent and resistant to degradation

Potential human toxicity

Man-made chemicals – not naturally occurring

Wide range of industrial and commercial applications and potential for exposure

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PFAS SOURCES

Processes

- Fluoropolymer coatings
- Plastics/polymers
- Teflon™, Stainmaster® carpets, Scotchgard™ Gore-Tex®
- Aqueous film forming foams (AFFF)
- Mist suppressants in metal plating operations
- Photolithography (semiconductors)
- Photography and film products

Product uses

- Food wrappers/paper, fast food containers, microwave popcorn bags, pizza boxes
- Non-stick cookware
- Water-resistant textiles, carpets, clothing, leather
- Ski and snowboard waxes
- Adhesives, paints, sealants
- Aviation hydraulic fluids
- Cleaning products
- Shampoo, dental floss, cosmetics

WHAT TYPES OF FACILITIES MAY BE IMPACTED?

Industrial facilities

- Chemical manufacturers
- Textile/carpet manufacturers
- Metal coating and plating sites

Facilities impacted by fires

- Rail yards
- Current and former DoD sites
- Airports
- Firefighting training areas
- Crash sites (planes and cars)

Others

- Landfills
- Water treatment systems

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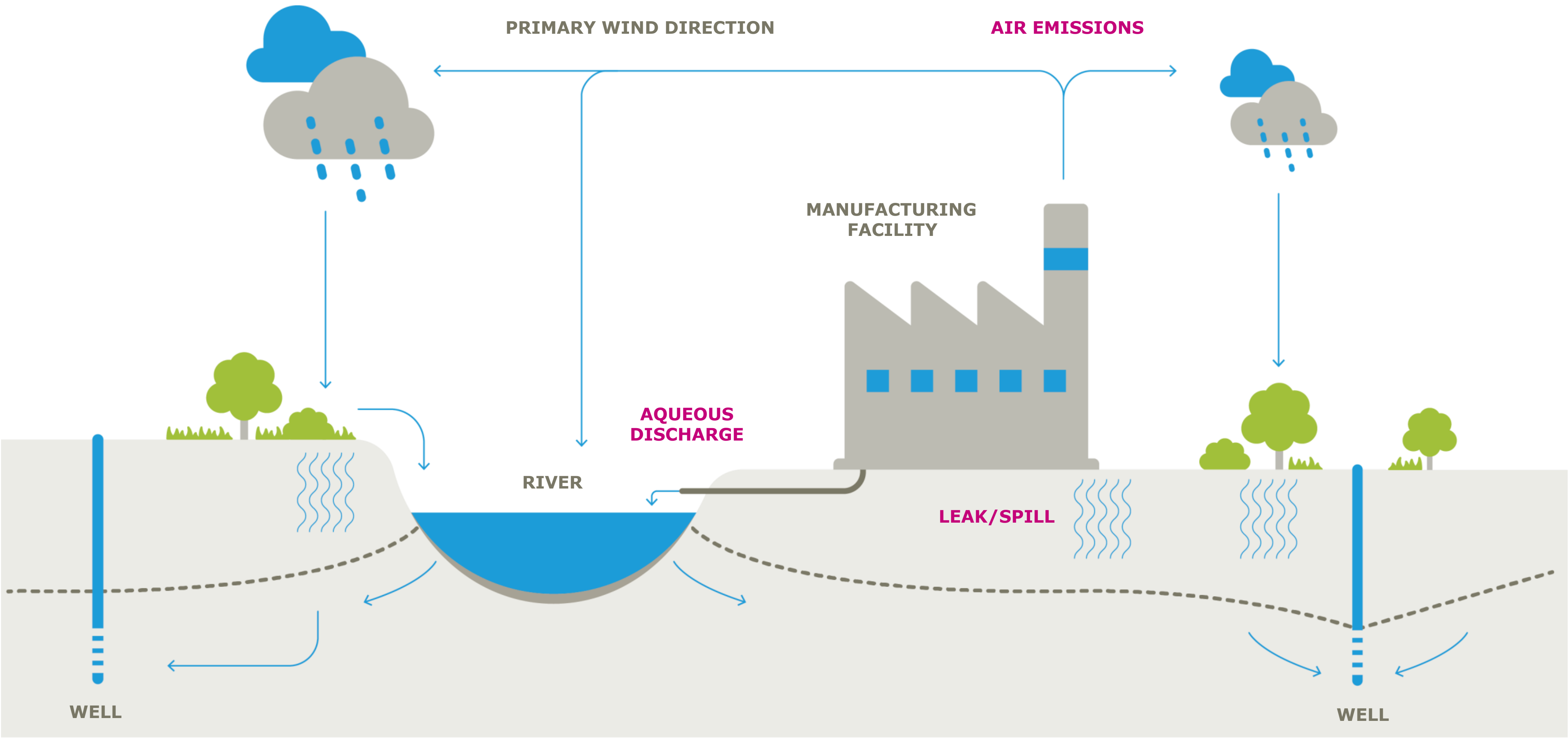
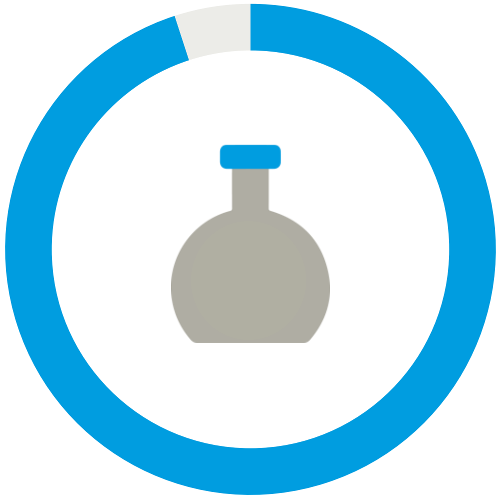
EXPOSURE & TOXICITY

MOVEMENT IN THE ENVIRONMENT



From Davis et al. 2007. Chemosphere 67: 2011-19.

EXPOSURE



+95%

of individuals sampled have detected PFAS in serum

Contact in the work place

Ingestion of food containing PFOA (theorized principal source for general public)

Ingestion of drinking water for individuals living in areas with PFAS-contaminated water supplies due to releases to the environment

Direct contact with products such as treated carpets and upholstery

ADME
ABSORPTION, DISTRIBUTION, METABOLISM & EXCRETION

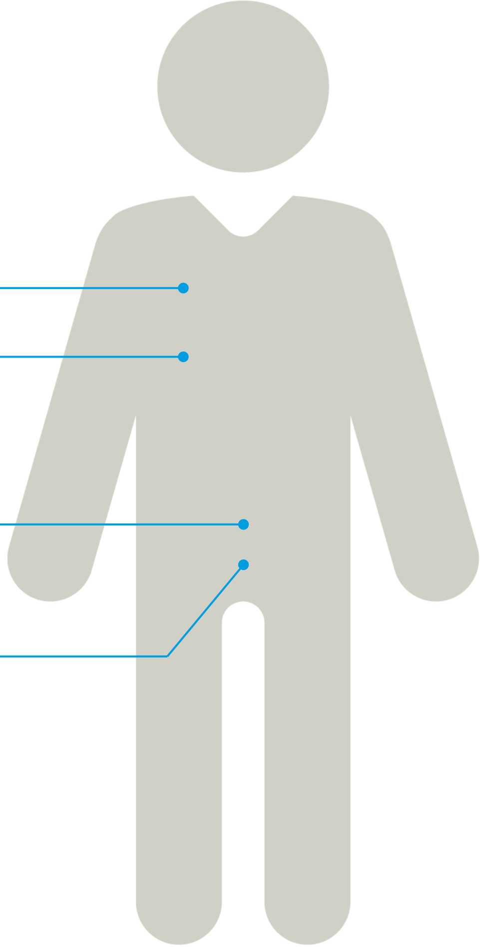
Readily absorbed

Not metabolized

Distributed predominantly to the liver and blood (serum)

Leaves the body through urine and feces

Reabsorbed to the body to an extent after excretion into urine and bile



Can cross the placenta and be present in breast milk

Median elimination half life for exposed community

= 840 days (2.3 years)

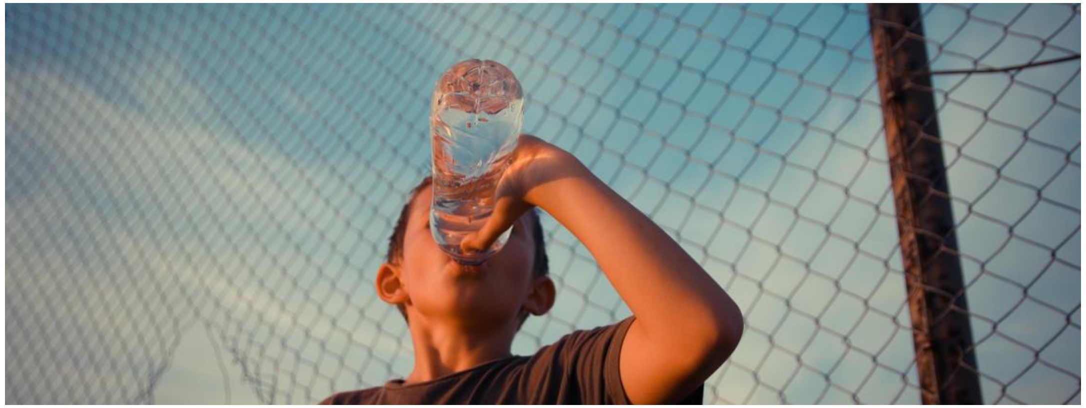
TOXICITY

Human – probable links

- Immunotoxicity – decreased vaccination response
- Thyroid disease
- High cholesterol
- Liver toxicity – increased liver enzymes
- Cancer – testicular, kidney
- Reproductive and developmental effects –
  - Pregnancy-induced hypertension and preeclampsia

Animal

- Developmental – body weight, hastened puberty
- Liver toxicity – necrosis, metabolism
- Kidney toxicity – weight
- Immune effects
- Cancer – liver, testicular, pancreatic



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REGULATORY RESPONSE

PFAS: A PERSPECTIVE FROM THE US

1940-1950s
Synthetic fluorinated chemicals developed as oil and water repellent

1950s-70s
3M disposed of PFC waste in Oakdale, Woodbury, Cottage Grove and Washington County, Minnesota

1966
AFFF was patented as a method for extinguishing liquid hydrocarbon fires and implemented by the DoD in 1969

1990s
USEPA receives information on PFOS and PFOA blood levels in general population

2000
3M stopped production of Scotchgard and ceased PFOS production at Cottage Grove plant

2004
PFCs found to have contaminated drinking water supplies in Minnesota

2005
$235 million lawsuit brought against DuPont over PFC contamination in the Ohio river

2006
USEPA launches PFOA Stewardship Program

2009
USEPA established drinking water health advisories of 0.4 ppb for PFOA and 0.2 ppb for PFOS

2013
USEPA initiates requirement for public drinking water supply monitoring of 6 unregulated perfluorinated compounds

2016
USEPA revises drinking water health advisory to 0.07 ppb for combined PFOA and PFOS

2017
DuPont settles toxic exposure law suit for $671 million

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PFAS: A PERSPECTIVE FROM THE US

Emerging Contaminants –
Perfluorooctane Sulfonate (PFOS)
and Perfluorooctanoic Acid (PFOA)
March 2014

Still considered an "emerging contaminant"

- Poses a real or perceived threat to human health or to the environment
- Not currently regulated or have regulations pending
- New source has been identified or a new exposure pathway to humans has been discovered
- New detection method or a new water treatment technology has been developed

2006 USEPA PFOA STEWARDSHIP PROGRAM

2002: PFOS last manufactured in US

PFOA Stewardship program: phase out of the manufacture and import of PFOA in the US

Goal: achieve a 95% reduction in emissions and product content by 2010

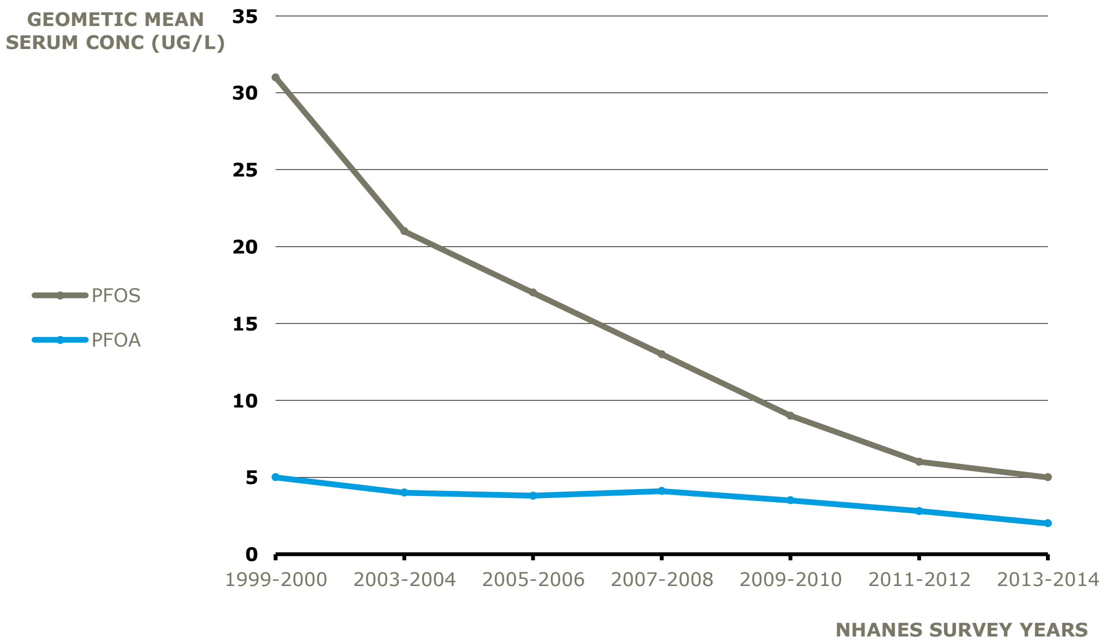
- PFOA
- Precursor chemicals
- Related higher homologues

Eliminate completely by 2015

2015 USEPA Progress Report – US Operations
(all 8 manufacturers reporting)

- %Reduction, PFOA emissions: 100%
- %Reduction, PFOA product content: 100%

PFAS LEVELS IN THE US POPULATION OVER TIME



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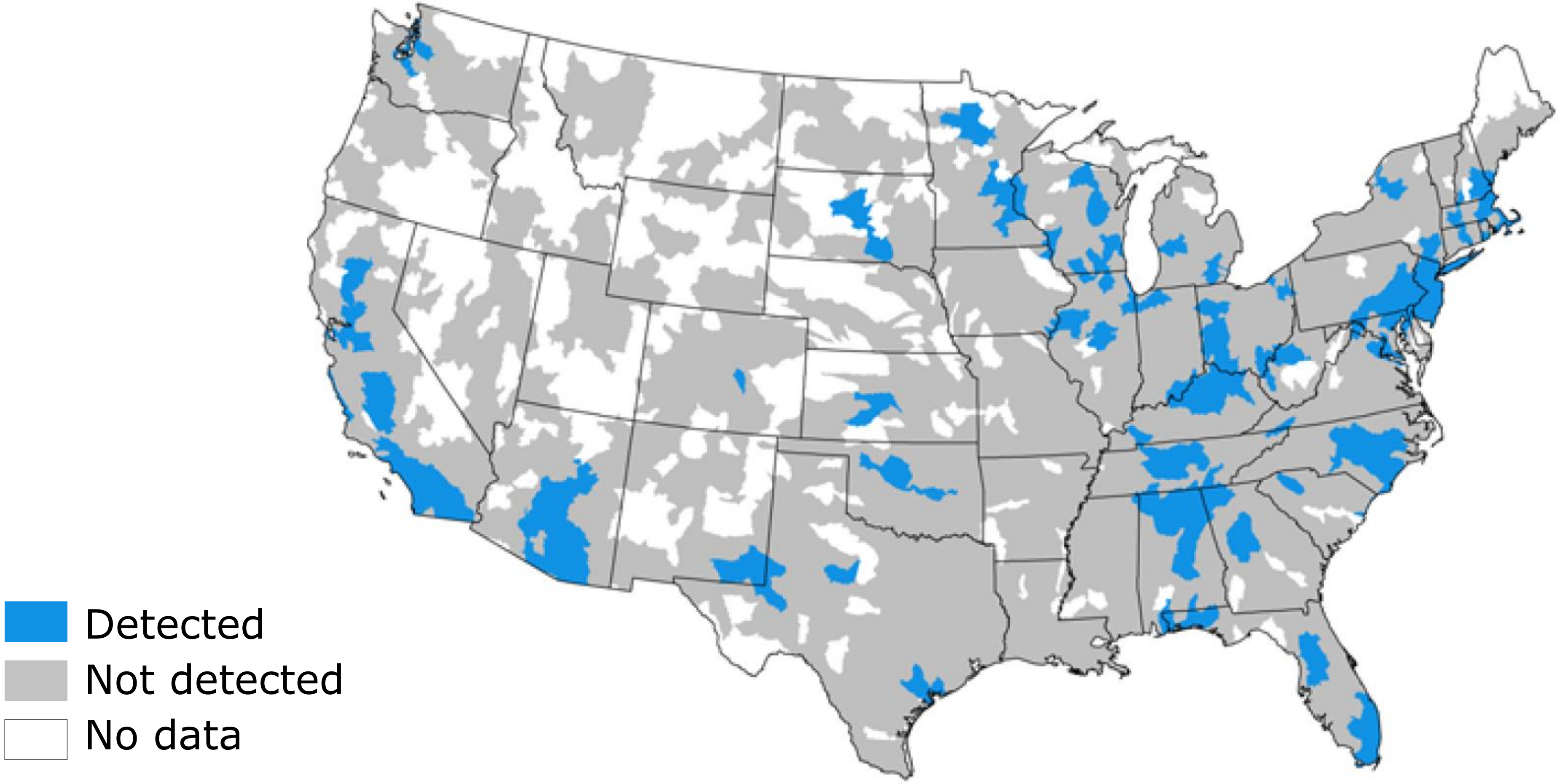
CONTINUING CONCERNS IN DRINKING WATER



From Hu et. al. 2015. Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. ES&T Letters. July.

CONTINUING CONCERNS

The New York Times

After Months of Anger in Hoosick Falls, Hearings on Tainted Water Begin

THE WALL STREET JOURNAL.

Concern Grows Over Tainted Drinking Water

Bucks County Courier Times

Federal agency responds to PFC investigation

Burlington County Times

Joint base: Two private wells in Ocean County tainted by PFOS, PFOA

From Hu et. al. 2015. Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. ES&T Letters. July.

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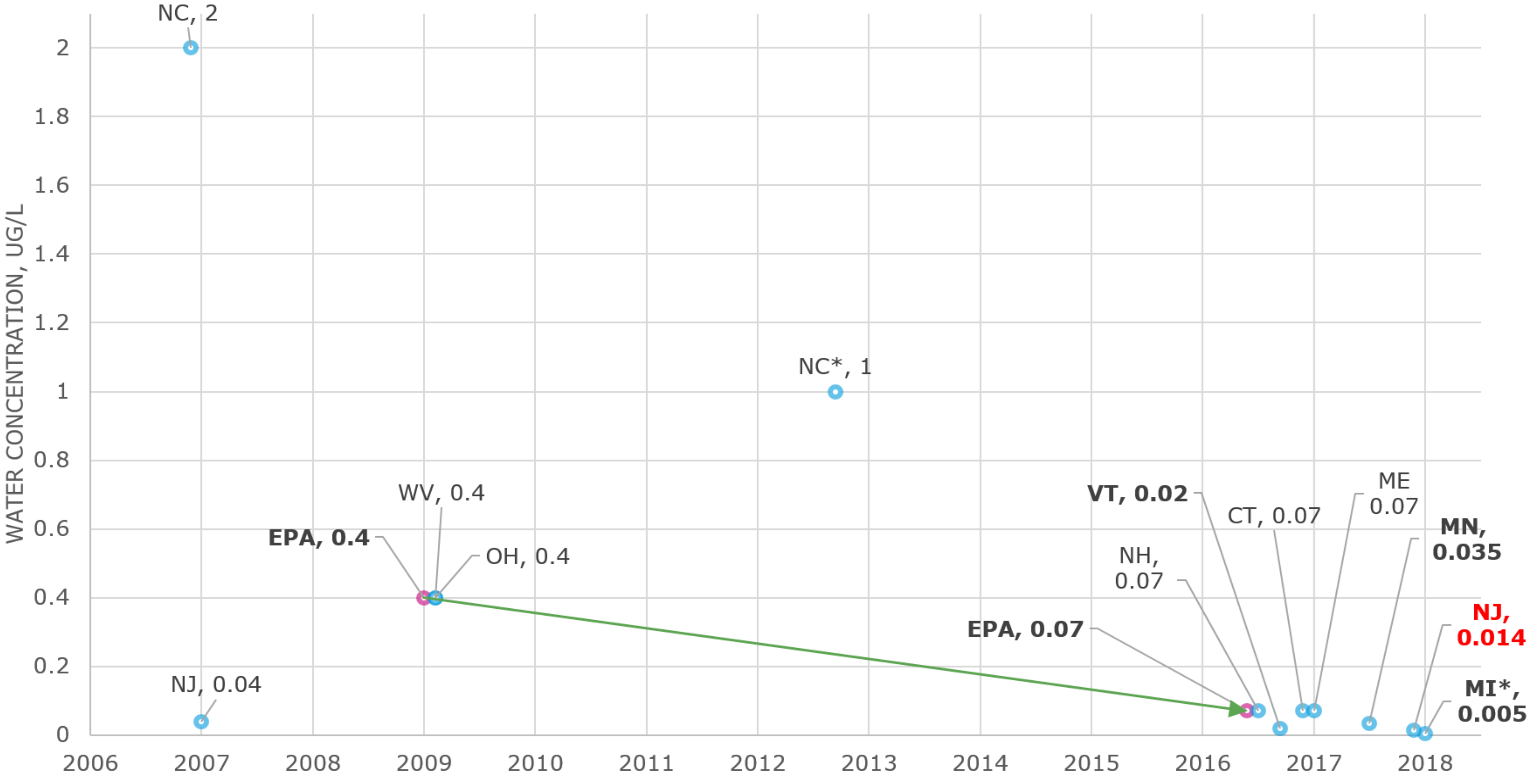
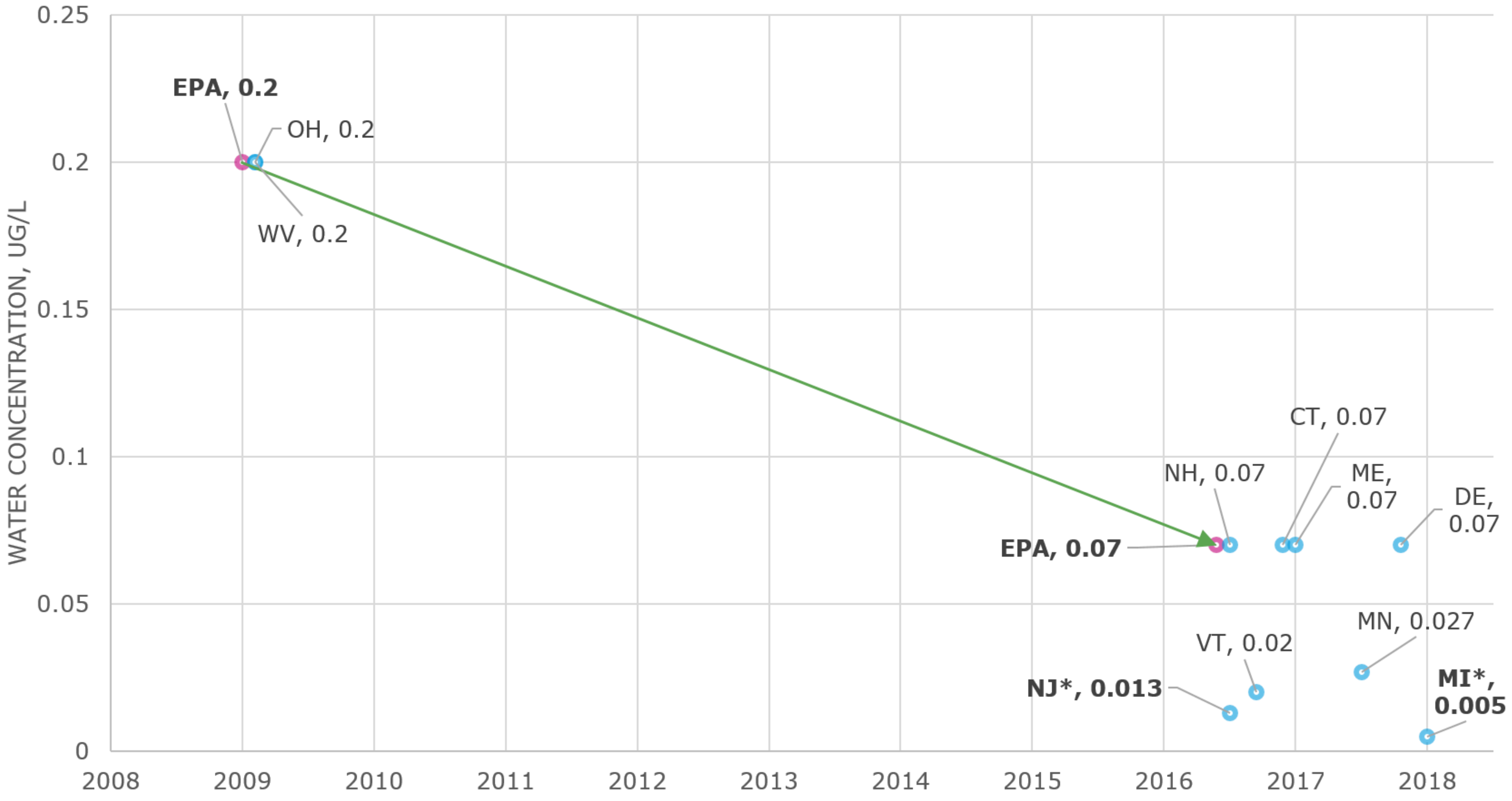
US PFOA DRINKING WATER HEALTH ADVISORIES



* Values are proposed standards

US PFOS DRINKING WATER HEALTH ADVISORIES



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* Values are proposed standards

US GROUNDWATER REMEDIATION STANDARDS

State	PFOS (ug/L)	PFOA (ug/L)	Source	Year	Type	Notes
Alaska	0.4	0.4	ADEC	8/25/2016	Individual	
Colorado	0.07	0.07	CO DPHE	5/16/2016	Combined	Proposed site-specific groundwater remediation standard
Iowa	0.07	0.07	IA DNR	5/19/2016	Combined	
Maine	0.56	0.13	ME DEP	2/5/2016	Individual	Remedial action guidelines
Michigan	0.07	0.07	MI DEQ	1/9/2018	Combined	
Texas	0.56	0.29	TCEQ	3/4/2016	Individual	Protective concentration level for remediation

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TRENDS IN REGULATORY GUIDANCE

Promulgation of standards for other PFAS

Short-chain compounds (e.g., PFBS, PFBA, PFHxS, PFHxA):

- IDEM 2017 soil and groundwater screening levels
- Wisconsin 2017 soil residual contaminant levels (RCLs)
- Texas 2017 soil and groundwater protective concentration levels (PCLs)

Long-chain compounds (e.g., PFNA, PFDA, PFUnDA, PFDoDA)

- Texas 2017 soil and groundwater PCLs
- New Jersey 2015 Interim GWQC for PFNA: **0.01 ug/L**

TRENDS IN REGULATORY GUIDANCE

Expanding regulatory values to other environmental media:

- Michigan 2015 surface water standards for PFOA and PFOS of **0.42 and 0.011 ug/L**

Proposition 65:

- PFOA and PFOS added for reproductive toxicity (developmental endpoint), effective November 2017

Food Packaging:

- Washington State passed HB-2658 banning PFAS in food packaging, effective in 2022

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LEGAL IMPLICATIONS

> “The health advisory value is not a legally enforceable federal standard and is subject to change as new information becomes available.”

- USEPA 2016

However…

LEGAL IMPLICATIONS

1 HAs are being used as guidance in state regulation

Health Advisory → **Public Scrutiny** → **Litigation**

2 Primary litigation target: groundwater contamination

DuPont and Chemours: $670.7M settlement for PFOA GW contamination against 3,500 individual plaintiffs (2/12/2017)

- This, after an initial settlement of $350M in 2004, brings total cost of litigation to over **$1B**

3M: $850M settlement for PFAS contamination in GW and NRD against Minnesota (2/20/2018)

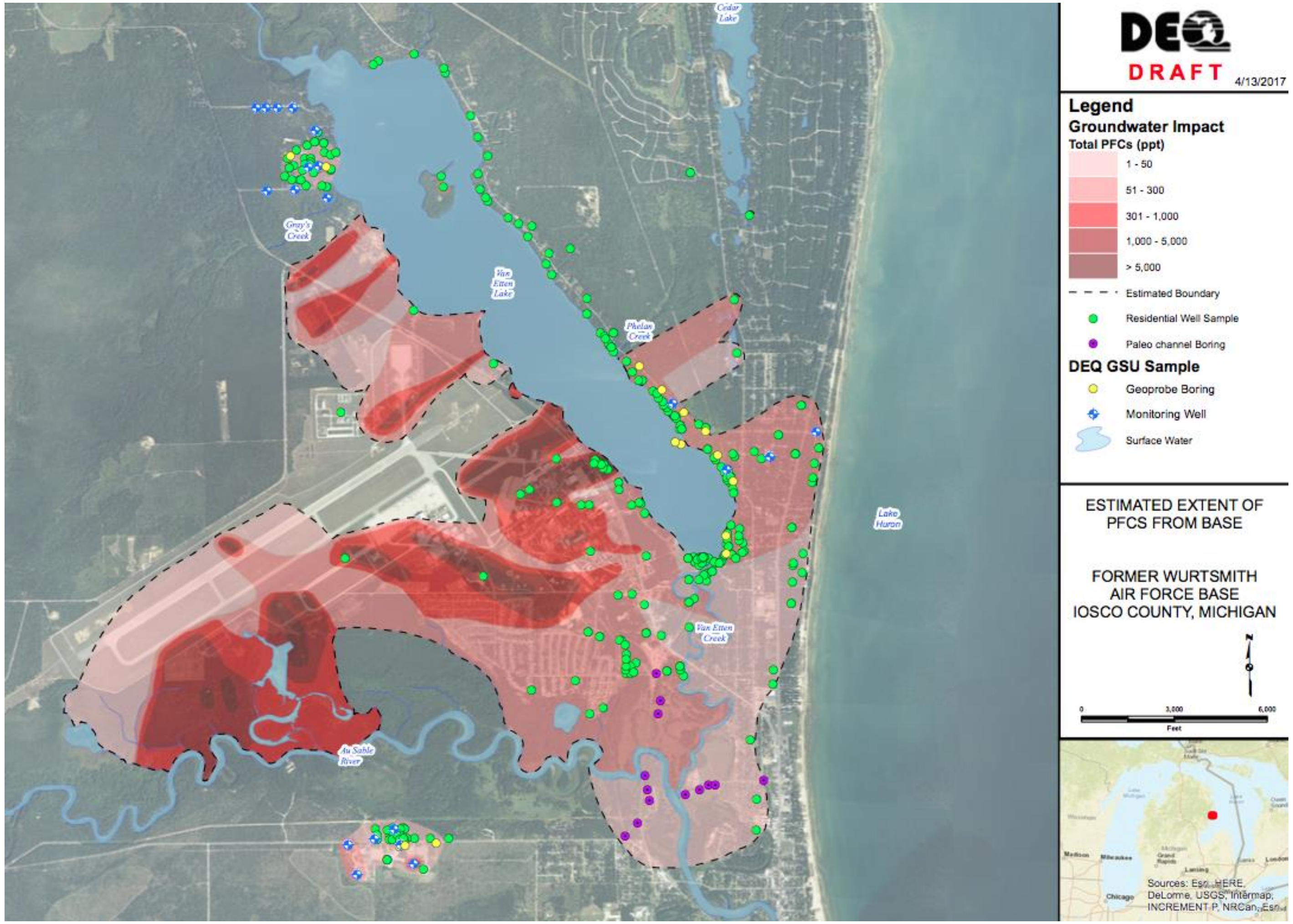
- 3rd largest NR recovery in the history of the US, largest settlement related to PFAS
- No admission of liability or wrongdoing

COMPLICATIONS

- Drinking water only one source of exposure – diet, indoor air and dust, soil, and consumer products make up approximately **80%** or more of all exposure pathways
- Shifting PFAS regulations – HAs based on animal studies
- Shifting PFAS use – short chain substitutions
- Long term and widespread use – who is at fault?
- Persistence and mobility in environment – remediation implications

GROUNDWATER REMEDIATION

TREATMENT CHALLENGES



Groundwater plumes can be very large and dilute, some over 1 mile in length

- High water solubility

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VIABLE GROUNDWATER TREATMENT OPTIONS

Activated carbon

- Granular, powder, liquid

Anion exchange (AIX) resins

Membrane treatment

- Reverse osmosis (RO)
- Nanofiltration

VIABLE GROUNDWATER TREATMENT OPTIONS
ACTIVATED CARBON TECHNOLOGIES

Pros

- Most utilized at full scale
- Highly effective (long-chain compounds >90% removed)
- Variety of forms (granular, powdered, liquid)

Cons

- Short-chain compounds break through quickly due to competition effects – new research contests this?
- Failure to regenerate or replace GAC can cause PFAS leaching
- Natural organic matter (NOM) can significantly decrease removal efficacy

Ex situ: Pump and treat

- Coal-based:
  - Calgon Filtrasorb 300, 600
  - Norit GAC300
- Coconut shell:
  - AquaCarb 1240C
- RemBind (adapted from soil technologies)

In situ: GW injections

- PlumeStop by Regensis

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VIABLE GROUNDWATER TREATMENT OPTIONS
ANION EXCHANGE RESINS

Pros

- Relatively inexpensive
- Effective at removing long-chain PFAS
- Utilized at large scale abroad

Cons

- PFSAs preferentially removed over PFCAs in full-scale applications
- Short-chain PFAS are not effectively removed
- Frequent resin changes likely required (conventional regeneration is ineffective for PFAS-containing resins)
- Requires additional pilot testing

MEMBRANE TECHNOLOGIES
REVERSE OSMOSIS

Pros

- Most effective form of treatment available
- Effectively treats short- and long-chain PFAS
- Proven at large scale (WTPs)

Cons

- Extremely costly
- Energy intensive
- Generates a brine/concentrate requiring further treatment or disposal

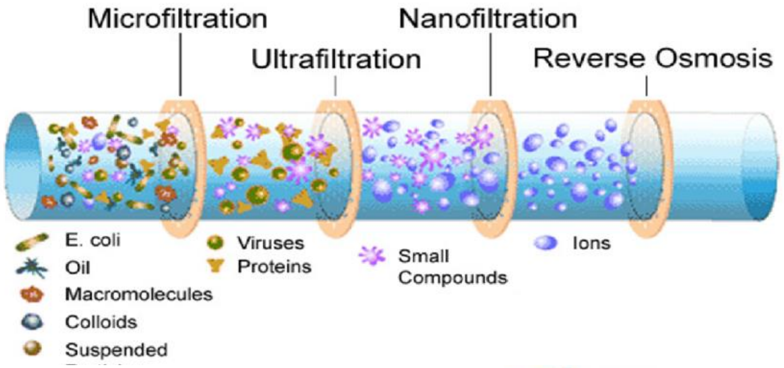
MEMBRANE TECHNOLOGIES
NANOFILTRATION

Pros

- Cheaper than reverse osmosis
- Removal efficiency not impaired by membrane fouling in bench-scale testing
- Extremely efficient, treats both short- and long-chain PFAS

Cons

- Bench-scale tested only
- Generates a concentrate requiring further treatment

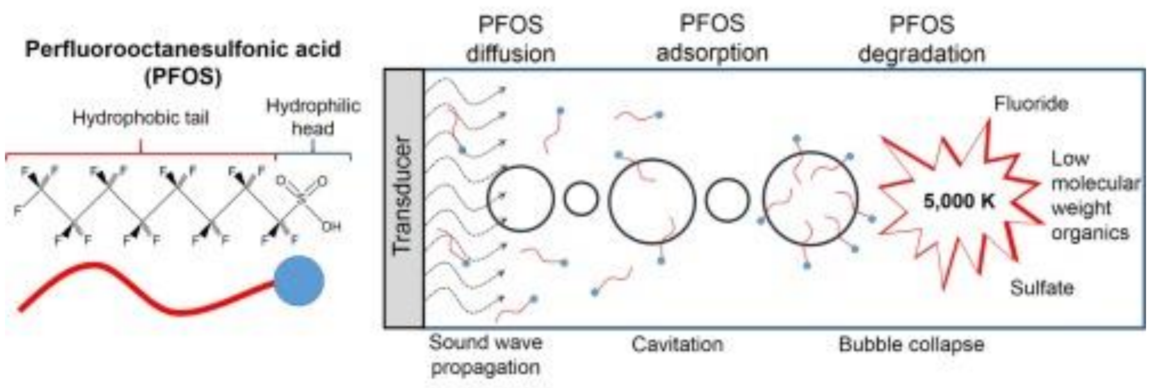


EMERGING OXIDATION/REDUCTION TREATMENTS

- Photocatalytic oxidation
- Photochemical oxidation/reduction
- Persulfate radical treatment
- Thermally-induced reduction
- Sonochemical pyrolysis

Bench scale

PFOS sonochemical degradation



Pros

- Sonochemical methods mineralize PFAS via pyrolysis

Cons

- Require additional testing
- Incomplete breakdown may generate harmful byproducts

INEFFECTIVE GROUNDWATER TREATMENT OPTIONS

Conventional treatment methods:

- Coagulation/flocculation
- Physical separation: micro or ultrafiltration, deep bed filtration, dissolved air flotation, sedimentation, granular filtration (sand)
- Disinfection (chloramination, UV, chlorination, ozonation)

Hydroxyl radical advanced oxidation processes (AOPs):

- Alkaline ozonation, peroxone, Fenton's reagent, UV/H2O2

Bioremediation: no known bacteria capable of full bioremediation

Soil aquifer treatment: little-to-no attenuation

PFAS REMOVAL EFFICIENCIES

Compound	Aeration	Coagulation dissolved air flotation	Coagulation flocculation sedimentation filtration	Oxidation (MnO_4, O_3, clo_2, cl_2, CLM, UV, UV-AOP)	Anion exchange	Granular activated carbon filtration	Nano filtration	Reverse osmosis
LMW PFCAs	🔴	🔴	🔴	🔴	🔴	🟡	🟢	🟢
HMW PFCAs including PFOA	🔴	🔴	🔴	🔴	🟡	🟢	🟢	🟢
LMW PFSAs	🔴	🔴	🔴	🔴	🟢	🟢	🟢	🟢
HMW PFSAs including PFOS	🔴	Unknown	🔴	Unknown	🟢	🟢	🟢	🟢

🔴 **Removal <10%**

🟡 Removal 10-90%

🟢 Removal > 90%

Abbreviations:
CLM: Chloramination; UV-AOP: UV Photolysis with Advanced Oxidation (Hydrogen Peroxide)
Adapted from: Treatment Mitigation Strategies for Poly- and Perfluoroalkyl Substances, WRF Report #4322, Prepared by Eric Dickenson and Christopher Higgins, 2016

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GROUNDWATER REMEDIATION SUMMARY

Technology	Status	*In situ*	*Ex situ*	Treatment type	Precursor concerns	Cost	Efficiency	Products	Other
Activated carbon (granular powdered liquid)				A				Calgon Filtrasorb 300, 600 Norit GAC300 AquaCarb 1240C PlumeStop Amended RemBind	Secondary treatment/disposal required for adsorptive media, not as efficient for short chain PFCAs
Anion exchange resins				A				Purolite FerrlX A33e Siemens A-714 Amberlite IRA-400 Dow MarathonA	PFSAs preferentially removed over PFCAs, less effective for short-chain PFCAs, requires resin replacement instead of regeneration
PerflourAd and filtration				A		?	?	Tersus PerflourAd (EU)	Precipitates PFAS from solution, followed by sedimentation and filtration, must dispose of flocked material
Reverse osmosis				S					Generates a brine that must be treated and disposed, very expensive
Nanofiltration				S					Still at testing stage, membrane fouling does not impact efficacy
Emerging oxidation/reduction		?		D		?	?		Conditions to destroy PFAS are difficult to apply at full scale for in-situ remediation
ISCOR – activated persulfate				D		?	?	ScisoR – smart combined in situ oxidation and reduction	Injectable into groundwater, developed by ARCADIS, pilot-tested

Abbreviations:
A: Adsorption; D: Destructive; S: Separation

SOME TAKEAWAYS

1. Unique properties → stable, mobile, and degradation resistant
2. Found in GW mostly in areas where used in manufacturing or at fire training sites
3. Exposure predominantly via food or in drinking water in areas with impacted drinking water supplies
4. Not metabolized in body, can remain in body for longer periods of time
5. Standards are changing → different agencies making different science-policy choices
6. PFAS litigation historically has involved groundwater, and led to costly outcomes

THANK YOU
QUESTIONS?

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